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OBSERVATIONS OF VOLATILE ORGANIC COMPOUND CONCENTRATIONS AND FLUXES FROM DIFFERENT ECO-SYSTEMS

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Academic dissertation

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Observations of volatile organic compound concentrations and fluxes from different ecosystems

Simon Schallhart

University of Helsinki, 2017

Abstract

Volatile organic compounds (VOCs) are emitted in vast amounts from biogenic and anthropogenic sources. They influence air quality and thereby human health. In the atmosphere VOCs can be oxidized to form compounds with lower volatility and form aerosol particles, which can affect the climate.

The basis of this thesis are VOC measurements with a proton transfer reaction time of flight (PTR-TOF) mass spectrometer. Its suitability for measuring the volatile organic compound spectra with 10 Hz resolution made it possible to calculate VOC exchange from different ecosystems with the eddy covariance method. The reliability of this method was determined by comparisons with other well-established ecosystem scale flux methods and upscaled emissions from leaf cuvettes. The measurements in this work resulted in the quantification of the total exchange in a broadleaf forest in Bosco Fontana, Italy and a conifer forest in Hyytiälä, Finland. By using a new automated method, 29 VOCs with exchange were measured in Bosco Fontana and 25 VOCs in Hyytiälä. These two ecosystems differ as the major terpene emissions are isoprene for the oak forest and monoterpenes for the Scots pine forest. Additional to isoprene and the monoterpenes, methanol, acetonitrile, acetaldehyde, acetone and acetic acid fluxes were measured at both sites. To identify the measured signals and determine error sources, fragmentation, possible losses and sources of different compounds were investigated. In a research stable in Switzerland, amine measurements and calibrations were performed to identify the source of trimethylamine. During measurements in Hyytiälä, the anthropogenic source of the measured butene was determined and a memory effect of acetic acid in our measurement setup was discovered.

Overall, this thesis addresses the potential of concentration and ecosystem exchange measurements using a PTR-TOF and challenges which arise during the measurements and data analysis. The obtained results are useful insights into the precursors and amplifiers (amines) of new particle formation and aerosol growth. Furthermore, the recorded direct total ecosystem exchange measurements expand the limited data available and can be used to improve and validate emission models.

Keywords: VOC, eddy covariance, concentration, volume mixing ratio, exchange, flux, PTR-TOF

Contents

1 Introduction 8
2 Methods 10
2.1 Measurement sites 10
2.2 Proton transfer mass spectrometry 12
2.3 Gas chromatography 17
2.4 Concentration measurements 18
2.5 Exchange and emission measurements 21
3 Challenges in measuring VOC concentrations 25
3.1 PTR sensitivity 25
3.2 Problems with fragmentation 27
3.3 Losses in the sampling system 28
4 Insights into VOC exchange 30
4.1 Ecosystem exchange 30
4.2 Challenges in the upscaling of emission 31
4.3 Improvements to the compound flux detection 33
4.4 Chemistry affecting fluxes 35
4.5 Deposition of methanol 36
4.6 Sources of amines in animal husbandry 38
5 Review of papers and the author's contribution 39
6 Conclusions 40
References: 42

List of publications

This thesis consists of an introductory review, followed by five research articles. In the introductory part, the papers are cited according to their roman numerals. All papers are reprinted under the Creative Commons License.

I Sintermann, J., Schallhart, S., Kajos, M., Jocher, M., Bracher, A., Münger, A., Johnson, D., Neftel, A., and Ruuskanen, T.: Trimethylamine emissions in animal husbandry, Biogeosciences, 11, 5073-5085, 2014.

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Abbreviations and nomenclature

a.s.l.	above sea level
bg	background
CCF	cross covariance function
cps	counts per second
Da	Dalton, unified atomic mass unit, $1.66 \cdot 10^{-27}$ kg
DW	dry weight
EC	eddy covariance
ETFE	ethylene-tetra-fluoro-ethylene
eTR	electron transfer reaction
FEP	fluorinated ethylene propylene
GC	gas chromatography
i.d.	inner diameter
LOD	limit of detection
MACR	methacrolein, $C_4H_7O^+$
MBO	2-methyl-3-buten-2-ol, $C_5H_{11}O^+$
MCP	multi-channel plate
MS	mass spectrometry
MVK	methyl vinyl ketone, $C_4H_7O^+$
n.i.	not identified
oVOC	oxidized VOC
PA	proton affinity
PAR	photosynthetically active radiation
PFA	perfluoroalkoxy alkane
PTFE	polytetrafluoroethylene
PTR	proton transfer reaction
Quad	quadrupole
SEM	secondary electron multiplier
SLP	surface layer profile
SMEAR	Station for Measuring Ecosystem-Atmosphere Relations
Th	Thompson, $1.04 \cdot 10^{-8}$ kg C^{-1}
Td	Townsend, 10^{-21} V m^2
TMA	trimethylamine
TMAO	trimethylamine oxide
TOF	time of flight
vDEC	virtual disjunct eddy covariance
VOC	volatile organic compound
w.c.	water cluster

1 Introduction

Volatile organic compounds (VOCs) surround us during our whole life. They are in the water and beverages we drink, in the food we eat and in the air we breathe. Most of them we do not notice actively, while others can be pleasant, like the smell of the forest, or unpleasant, like the odor of a manured field. Most of these odors and smells are VOCs, which are mainly emitted by natural ecosystems like forests, meadows, swamps and wetlands. These biogenic emissions account for approximately 1100 Tg y^{-1} without counting methane (Guenther et al., 2012). The most emitted VOC is isoprene (50%), followed by the group of monoterpenes (15%), methanol (10%) and acetone (5%). The functions of these biogenic emissions are various. Emissions of VOCs help the plants to relieve oxidative- or heat stress, are used in plant signaling, are direct defenses against herbivores and can also attract herbivore enemies (Holopainen and Gershenzon, 2010).

Many VOCs are anthropogenic, mainly by-products emitted by combustion or biomass burning. Overall, these emissions are approximately one order of magnitude lower than the biogenic and amount to 186 Tg y^{-1} (EDGAR, 2005).

In the atmosphere VOCs (Fig. 1) are crucial for air chemistry, as they react with e.g. ozone (O_3), the hydroxyl radical (OH) or NO_3 (nitrate radical) and form oxidized products, i.e. oxidized VOCs (oVOCs). Estimations of the number of different VOCs go up to 1 000 000 compounds just with ten carbon atoms or lower (Goldstein et al., 2007). This huge amount

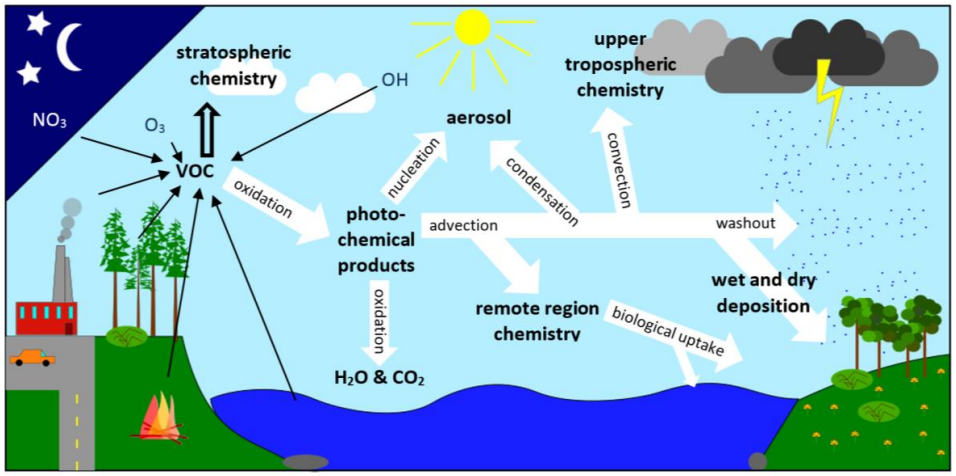

Figure 1: Model of the possible pathways of VOCs in the atmosphere, adapted from Williams and Koppmann (2007).

of different compounds, as well as their possible short atmospheric lifetimes and low concentrations make it very challenging to measure VOCs. Their concentration is determined by their sources and sinks. Depending on the properties (e.g. volatility, solubility), the compounds have different sink terms. Low volatility compounds can easier form or grow aerosol or be lost due to dry or wet deposition. Other compounds oxidize to CO_2 and water or are

lost to biological uptake. Due to these complex source, sink and reaction pathways, measurements of VOC exchange between biosphere and atmosphere are crucial for understanding the complex processes of atmospheric chemistry.

Aerosol formation is the process where new aerosol particles are created from vapors of, e.g., sulfuric acid, ammonia, amines or oxidized VOCs (Kulmala et al., 1998 and 2004; Kirkby et al., 2011; Almeida et al., 2013; Jokinen et al., 2015; Kirkby et al., 2016). Chamber studies in European Organization for Nuclear Research **(**CERN) have shown that amines can rapidly form stable clusters with sulfuric acid, making the compound a very potent source of sub 3 nm particles (Almeida et al., 2013), while particle formation from purely biogenic vapours can take place in environments with low sulfuric acid pollution (Kirkby et al., 2016). The contributing vapors vary in different ecosystems (marine, coastal, rural or urban) and are not entirely identified (Zhang et al., 2011; Sipilä et al., 2016).

The growth of these newly formed particles to climate relevant cloud condensation nuclei sizes is dominated by organic matter (Saxena and Hildemann, 1996; Riipinen et al., 2011). Jimenez et al. (2009) showed that in most of the investigated 26 measurement sites around the world, even in urban sites, organics dominate the aerosol composition. This organic matter can be formed by oxidation products of various VOCs, which can contribute to the growth of the existing aerosol substantially. Ehn et al. (2014) discovered the highly oxidized molecules, which are formed by monoterpene oxidation under similar conditions as found in a boreal forest, and are responsible for the aerosol growth. This growth of aerosol is important for the formation of cloud condensation nuclei (Kerminen et al., 2012), which then can affect the cloud properties such as brightness and lifetime (Boucher et al., 2013).

Overall, VOCs form highly oxidized molecules which are essential for the formation and growth of aerosol (Tröstl et al., 2016) and are thereby, relevant for the climate. However, the role of biogenic and anthropogenic VOCs and their impact on aerosol formation and growth are still uncertain (IPCC, 2013) and need further investigation.

The main objectives of this thesis are:

- To quantify ecosystem exchange of VOCs in different ecosystems measured by eddy covariance (**paper II, III** and **V**) and compare it with other well-established flux and emission measurement methods.
- To investigate a new automatic method for fast and objective detection of fluxes of several hundred VOCs (**paper II**)
- To identify interferences (e.g. chemistry, fragmentation) with VOCs measured by proton transfer reaction time of flight mass spectrometry (**paper I** to **V**)
- To determine the amine source from cattle at a research stable (**paper I**)

2 Methods

2.1 Measurement sites

The work presented in this study was performed at three measurement sites in Switzerland, Italy and Finland. The sites include a research stable where VOCs originating from cattle were investigated, an isoprene emitting broadleaf forest in central Europe, as well as a boreal forest, which emits monoterpenes. Additional laboratory measurements were performed at the Agroscope ISS, Zurich, Switzerland.

Agroscope Posieux

The ambient measurements in **paper I** were conducted at the Federal Research Station in Posieux, Switzerland (Fig. 2; 46.7692° N, 7.10653° E; 640 m a.s.l.). The cattle barn sheltered 60 dairy cows with an average weight of 680 kg (annual average milk production of 8500 kg per cow). The breed of the cows is Fleckvieh and Holstein Friesians, and their diet consisted of concentrated rations of a cereal mix, maize silage and grass from the pasture. During the day the cows spent most time on the pasture. In the morning and in the afternoon they were milked, before and after which the cows spent 3 to 5 h in the barn complex (Fig. 2). The measurements were performed in the barn and in the yard with and without the cows. The instruments were housed in an air conditioned trailer (Fig. 2) and air was sampled through a 24 m long 12.7 mm outer diameter perfluoroalkoxy alkane (PFA) line (more information in Sect. 3.3). The measurements at this site were performed from 25.07.2011 to 06.08.2011.

Figure 2: Pictures of the measurements in the barn, where the cows were fed (left). The inlet is marked with a red circle. The cows waiting in the yard for the milking (middle). All instruments were inside an air conditioned container (right).

Bosco Fontana

Bosco Fontana (Fig. 3; 45.19783° N, 10.74201° E; 25 m a.s.l.) is a nature reserve of 233 ha in the northeast of the Po Valley, Lombardy, Italy. The main tree species are *Quercus cerris* (turkey oak), *Quercus robur* (pedunculate oak), *Quercus rubra* (northern red oak) and Carpinus betulus (hornbeam; Dalponte et al., 2008). The typical tree height is between 26

and 28 m. The temperatures varied from 18 to 32°C during the measurements. The climatological mean annual temperature is 13.3°C and the mean annual precipitation is 834 mm. Most of the surrounding area is agricultural land and small roads. Mantua, located 8 km in the southeast, is the largest city in the vicinity with 48 000 inhabitants. The campaign lasted from 15.06.2012 to 06.07.2012 and was the basis for **papers II** and **III**. The instrument was installed in an air conditioned container, with the inlet sampling air from the 32 m high scaffolding tower (Fig 3).

Figure 3: Satellite picture showing Bosco Fontana (dark green area) with the measurement tower, the surrounding agricultural area and Mantua (left; imagery© 2015 Cnes/Spot Image, DigitalGlobe, European Space Imaging, Landsat, map data © 2015 Google). Photo of the scaffolding tower and the air conditioned container (right).

Hyytiälä

Measurements used in **paper IV** and **V** were conducted at the SMEAR II (Station for Measuring Ecosystem-Atmosphere Relations) in Hyytiälä, southern Finland (Hari and Kulmala, 2005; Ilvesniemi et al., 2010). The approximately 50 year old stand at the station (Fig. 4) is dominated by *Pinus sylvestris* (Scots pine), while *Picea abies* (Norway spruce) covers 15% of the forest. Additional tree species are *Betula pendula* and *Betula pubescens* (silver and downy birch, respectively), *Populus tremula* (trembling aspen), *Sorbus aucuparia* (rowan) and *Salix caprea* (goat willow; Williams et al., 2011). The tree height is around 18 m, while the inlet was attached to a scaffolding tower at a height of at 23 m (61.84740° N, 24.29515° E; 180 m a.s.l.). Pirinen et al. (2012) reported the climatological mean annual temperature at the Hyytiälä station to be 3.5°C and the mean annual precipitation to be 711 mm. Additionally to various meteorological, trace gas and aerosol measurements (e.g. Kulmala et al., 2013 and references therein), VOCs have been investigated at SMEAR II for almost two decades (Rinne et al., 2000), and emissions have been measured by gas chromatography and proton transfer reaction mass spectrometry (Sect. 2.2 and 2.3) with various flux measurement methods (Sect. 2.5). The measurements for **paper IV** were recorded between

11.06.2015 and 27.06.2015, while data for **paper V** was measured between 14.04.2013 and 24.06.2013.

Figure 4: The SMEAR II station with the surrounding boreal forest (left picture: imagery©2017 Google, Map data ©2017 Google). The white circles mark the measurement tower, where the flux measurements for **paper V** were conducted. The measurements for **paper IV** were recorded in the container area (orange circle).

2.2 Proton transfer mass spectrometry

Proton transfer reaction (PTR) is a widely used ionization technique in atmospheric research (Hansel et al., 1995; de Gouw and Warneke, 2006), where hydronium ions (H_3O^+) are used to charge and measure VOCs (R):

$$R + H_3O^+ \longrightarrow RH^+ + H_2O, \quad (1)$$

The key parameter for this reaction is the proton affinity (PA), which determines whether this reaction can occur. If the PA (Table 1) of a molecule R is lower than the PA of water, 691 kJ mol^{-1}, it will not receive the proton and will not get charged. This is the case for the most abundant molecules in the air, e.g. N_2, O_2 and CO_2. In the PTR-MS instrument the hydronium ions are created in the ion source, where water vapor is guided by low pressure into the hollow cathode (Fig. 5). There the natural ionization from radon and cosmic rays, together with the high electrical potential applied to the cathode initiate a plasma. In this plasma all different fragments of H_2O are ionized. Negative ions will be lost to the walls, while positive ions will form the hydronium ions. Additionally, water clusters and some impurities (e.g. O_2^+, NO^+) are formed. These ions are guided to the drift tube where the ions are mixed with ambient air. Here organic compounds with a PA exceeding 691 kJ mol^{-1} will be ionized. Compounds with a PA close to that of water, like formaldehyde and hydrogen cyanide, will be charged less efficiently (Inomata et al., 2008; Knighton et al., 2009).

The drift tube has controlled values for electrical potential, pressure and temperature, which define the energy per ion, E/N. To keep the E/N constant over the measurement period and limit losses to the surface in the instrument, the ion source and drift tube are inside an oven, which is kept on a constant temperature (150°C in **paper I** and 60°C in **papers II** to **V**). A typical setting for the E/N is around 130 Td (Townsend; 10^{-21} V m^2).

PTR instruments are known for their soft ionization that is limiting fragmentation, and providing high sensitivity, which enables the instrument to measure at limits of detection of around 0.4 to 40 ppt at 30 min time resolution (**paper II**). However, some compounds fragment during the ionization process, which is discussed in Sect. 3.2.

Table 1: Proton affinities of different compounds found in the atmosphere.

Elem. composition	Proton affinity [kJ/mol]	Name
O_2	421	oxygen
N_2	494	nitrogen
CO_2	541	carbon dioxide
CH_4	544	methane
H_2O	**691**	water
HCN	713	hydrogen cyanide
CH_2O	713	formaldehyde
C_6H_6	750	benzene
CH_4O	754	methanol
C_7H_8	784	toluene
C_8H_{10}	796	o-xylene
C_3H_6O	812	acetone

Time of flight

The name "time of flight" (TOF) describes the principle of operation, where charged molecules need to pass a certain distance while the time is measured. This time is converted into mass by using the relation:

$$\frac{m}{z} = \left(\frac{t - t_0}{a}\right)^2, \tag{2}$$

where $\frac{m}{z}$ is the mass (m) to charge (z) ratio, which equals m, as multiple charging does not occur with the PTR method ($z = 1$). The remaining parameters, t_0 and a, are calibration factors. These calibration factors are used to correct shifts in the mass scale, which are caused by e.g. changes in temperature of the TOF mass selector or uncertainties in the extraction. This change in temperature affects the length of the flight path and, therefore, the time of flight. The two calibration factors are determined by selecting known mass peaks in the measured spectra, by assigning them the known exact mass and by fitting Eq. (2) to the data.

In the last decade the TOF mass selector became very popular in atmospheric mass spectrometry (e.g. DeCarlo et al., 2006; Graus et al., 2010; Junninen et al., 2010; Jokinen et al., 2012). It has a high mass resolution ranging up to 4500 (full width at half maximum), which enables the instrument to separate compounds with different elemental compositions. The fraction of ions that reach the detector in relation to the ions that enter the TOF is very good when compared to other mobile mass selectors.

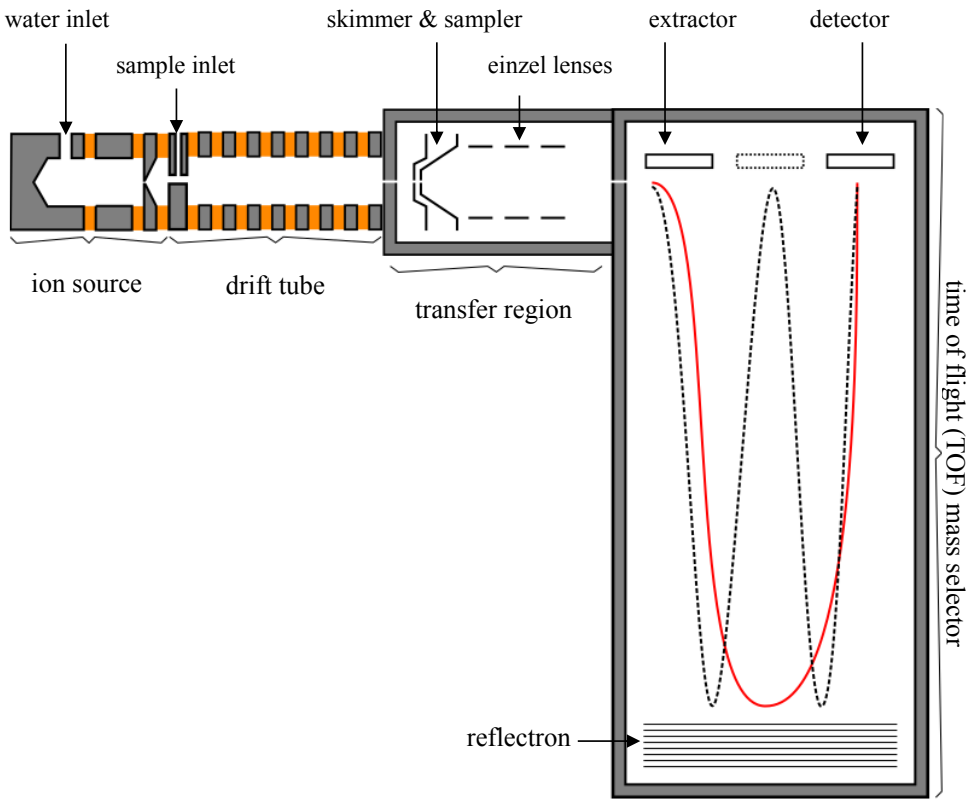

Figure 5: Schematic drawing of the PTR-TOF, showing the ion source, drift tube, transfer region and the TOF mass selector.

The flight path inside the instrument is V-shaped and electric fields are used to keep the ions on their way. First, the ions are accelerating orthogonally (to their flight path) with an extractor, where they fly in a high vacuum (~5 10^{-10} bar) to the reflector. There they are reflected and focused on the detector. The detector consists of two multi-channel plates (MCPs) where the angled channels are rotated 90° from each other, also known as chevron alignment. The signal from the detector is amplified and recorded by a time-to-digital converter. The difference between the activation time of the extractor and the time the ions were detected at the MCPs is called the time of flight. This operation mode allows the TOF to acquire data from hundreds of different mass peaks with up to 10 Hz time resolution. The time of flight is then converted into a mass by using Eq. (2).

To identify the compound, the nominal mass and the mass defect are used (Table 2). The mass defect of a compound is the difference of the measured mass to the closest unity mass. As the TOF measures all ions simultaneously, offers a good transmission and is capable of measuring full mass spectra in sub-second integration times. This makes it possible to search for compounds of interest, years after the actual measurements, which was not possible in

Table 2: Masses and mass defects of several elements and an electron. Da stands for Dalton ($1.66 \cdot 10^{-27}$ kg).

element/particle	mass [Da]	mass defect [Da]
C	12.0000	0
H	1.0078	+0.0078
O	15.9949	-0.0051
N	14.0031	+0.0031
F	18.9984	-0.0016
P	30.9738	-0.0262
S	31.9721	-0.0279
e^-	0.0005	+0.0005

older PTR-MS instruments. The high mass resolution of over 4500 (full width half maximum) enables it to separate isobaric compounds, however, it is not capable of distinguishing isomeric compounds. One drawback of the TOF mass selector is that it collects spectra, where every mass peak must be fitted and integrated, before even preliminary concentration values can be used (Fig. 6). This makes data post processing and quality assurance time consuming.

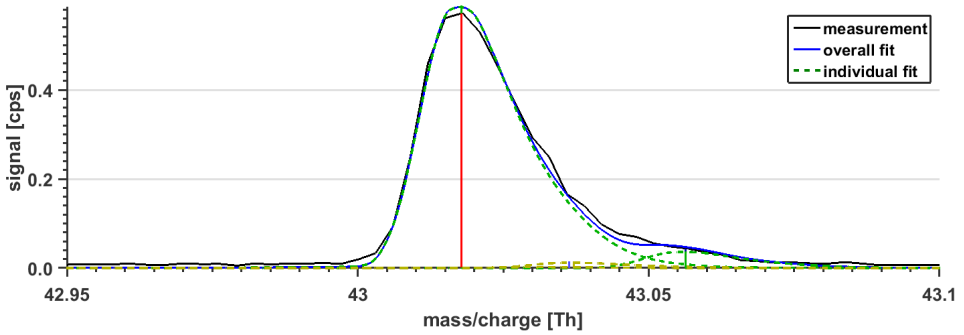

Figure 6: Fitting of $C_2H_3O^+$ and an unidentified peak at 43.0564 Th. The vertical red and green bars show the center of the fit, which is close to the exact mass of the measured compounds. This 30 min spectrum was recorded on the 13.05.2013 at 17:00 in Hyytiälä.

PTR-TOF

The instrument that combines the PTR ionization with the TOF (H-TOF, Tofwerk AG) mass selector is called a PTR-TOF. The main instrument used in this thesis (**papers I-V**) was the PTR-TOF 8000 (Ionicon Analytik GmbH), and it is described in Graus et al. (2010) and Jordan et al. (2009).

The good sensitivity of the PTR-TOF in connection with the high measurement frequency enables it to be used in eddy covariance measurements (Sect. 2.5). The first publication using a PTR-TOF was by Blake et al. (2004), while the first non-technical publication of ambient measurements was published by Ruuskanen et al. (2011).

PTR-TOF data processing

A major challenge is the analysis of the vast amount of data created by the PTR-TOF. For this two different routines, both coded in Matlab (Mathworks) were used: The tofTools (**papers I, IV** and **V**) were coded by Heikki Junninen and the tofTools team from the University of Helsinki. The PTR-TOF Analyzer 2.45 (**papers II** and **III**) was written by Markus Müller, while working at the University of Innsbruck and IRCELYON. The routines are described in detail in Junninen et al. (2010, 2013) and Müller et al. (2010, 2013), respectively. These routines use the raw spectra created by the TOF-MS to create the time trace of the fitted peaks. The main parts of the routines are similar and are summarized below.

At first the spectra are integrated to the desired data integration time, which was 30 min for concentration measurements in **paper I** to **IV** and 10 Hz in **paper II, III** and **V**. Then the mass scale was calibrated by using known single peaks, which were always present in the spectrum and not saturated. In this study the used mass scale calibration compounds were the isotope of the primary ion ($H_3[^{18}O]^+$), the isotope of the first water cluster isotope ($H_5O[^{18}O]^+$), acetone ($C_3H_7O_1^+$) and trichlorobenzene ($C_6Cl_3H_4^+$). Trichlorobenzene was added steadily from a reservoir, which was connected to the inlet via a capillary. This artificial addition of a mass scale calibration compound was necessary as in the ambient air there are not always peaks present above 150 Th (Thompson, $1.04 \cdot 10^{-8}$ kg C^{-1}). The calibration of the mass scale is needed for an accurate calculation of a mass of a compound from its time of flight (Eq.2). It also corrects for temperature fluctuations, which cause changes in the length of the flightpath and therefore shifts on the mass axis. This correction is very important for the identification and the correct fitting of the peak.

Finally a peak list can be created from a selected time window and the mass peaks are fitted. If the compounds of interest are already known, it simplifies the process since only a predefined limited set of data will be used. However, if all the measured peaks should be analyzed, the peaks have to be added to the peak list. To do so, the minimum, maximum and average values of each bin were used, to see which compounds are always present and if there are some peaks which just rise sporadic (Fig. 7).

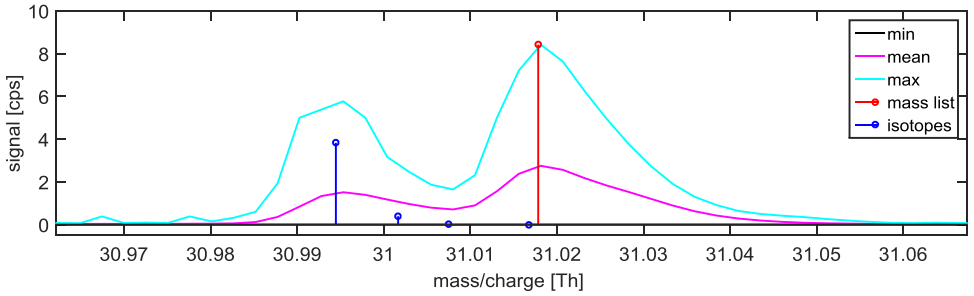

Figure 7: Minimum, mean and average signal around mass 31 Da. The first peak is an isotope of NO^+ while the second peak is the protonated formaldehyde. The signal has the unit counts per second (cps).

PTR-Quad and eTR-Quad

The PTR-Quad has the same source and drift tube as the PTR-TOF, but uses a quadrupole mass selector. The PTR-Quad also uses a different detector, a secondary electron multiplier (SEM). Due to the simpler mass selector, the PTR-Quad is less expensive. The quadrupole selects one mass after another for analysis, so its duty cycle and time resolution are the highest when just few compounds are measured. Furthermore, it has a unit mass resolution, and therefore is not able to differentiate between isomeric compounds. This fact makes the data handling and processing much easier, as there is no high precision peak fitting required, and the time traces of different compounds are a direct output of the instrument. At the same time, however, it is more challenging to identify the compound allocated to the signal.

Another disadvantage is the poor duty cycle of the quadrupole. As it disregards all the other ions except the measured one, the measurement time increases depending on the number of measured masses. The compounds of interest are preselected to maximize data coverage and counting statistics, and, therefore, a compromise between the data quality of a compound and the quantity of the compounds needs to be made. This is especially important when measuring direct fluxes, as the amount of data points influences the uncertainty (see Ecosystem exchange: direct methods in Sect. 2.5).

In **paper I** a custom made electron transfer reaction-quadrupole (eTR-Quad) mass spectrometer was used to measure the ammonia concentrations. The basic characteristics are similar to that of the PTR-Quad. However, when using a water plasma in the ion source, NH_3 is also created, which leads to a high instrumental background (Norman et al., 2007). This background drastically increases the limit of detection, which can be problematic for ambient ammonia measurements. When using oxygen as source gas, the instrumental ammonia background is greatly reduced, while the produced O_2^+ ions charge ammonia and VOCs by the electron transfer:

$$NH_3 + O_2^+ \longrightarrow NH_3^+ + O_2 \quad (3)$$

To minimize the wall losses and, therefore, increase the sensitivity of the eTR-Quad, the ion source and the drift tube were heated to 200°C and metal surfaces in the drift tube were minimized (Sintermann et al., 2011). Minimizing wall losses is especially important for observation of highly sticky compounds such as ammonia and amines.

2.3 Gas chromatography

Gas chromatography mass spectrometry (GC-MS) is widely used in the atmospheric sciences (Harris, 2007; Koppmann, 2007) and is sometimes called the golden standard of measuring VOCs. The first developments with chromatography started around 1910 in Russia and were developed further continuously, leading to a Nobel Prize in chemistry 1952 for Archer John Porter Martin and Richard Laurence Millington Synge.

In the GC technique, the VOCs are first collected for several minutes up to several hours with cold traps or adsorbent tubes. The collected VOCs are then extracted from the traps or tubes by thermal desorption units. Subsequently, the VOC sample is guided through a column by the carrier gas. Depending on the chemical and physical properties, as well as the interaction with the inner coating of the column, different compounds need different retention times to pass through the column. After the column a detector records the time and intensity of each compound. From the retention time, the compound can be identified, and the concentration can be determined from the intensity.

Offline GC-MS

In **paper III** the samples were collected offline by using Tenax tubes (Supelco, USA) to trap the VOCs emitted from a Mediterranean oak forest by using a plant cuvette. The samples were then later analyzed in the laboratory using a Perkin Elmer Clarus 580 gas chromatograph with a thermal desorber Turbo Matrix (Perkin Elmer Inc.) and a Clarus 560 mass detector. An Elite-5-MS capillary column with 30 m length, 250 µm diameter and 0.25 µm film thickness separated the different VOCs by using helium as a carrier gas. To ensure the quality of the samples, a steady sampling flow and storage of the samples together with blank samples at low temperatures are necessary.

Online GC-MS

In **paper IV** an online GC-MS was measuring ambient air, without any need for further laboratory analysis. To achieve this, the VOCs in the ambient air were collected for 1 h on a cold trap (U-T17O3P-2S, Markes International Ltd.) in the in situ thermal desorption unit (Unity 2+ Air server 2, Markes International Ltd.). An Agilent 7890A (Agilent Technologies) gas chromatograph using a 30 m DB-WAXetr column (J&W 122-7332, Agilent Technologies), which had an inner diameter of 250 µm and a film thickness of 0.25 µm, separated the compounds. Helium was used as a carrier gas and the separated compounds were detected by an Agilent 5975C (Agilent Technologies) mass spectrometer.

2.4 Concentration measurements

The volume mixing ratio (also referred to as concentration) describes the volume of a compound divided by the volume of the mixture. Atmospheric VOC mixing ratios measured with PTR-MS are normally in the range of sub-ppm ($<10^{-6}$) to ppt (10^{-12}), lower concentrations are under the detection limit. The measured concentrations can be transported over thousands of kilometers over the globe, while others react within meters from their source. Therefore, the concentration measurement footprint depends on the atmospheric lifetime of the specific compound. VOC concentrations play a key role in atmospheric modelling, air quality and health issues.

A reliable determination of concentrations requires a calibration and zero measurements. In the following section, the necessary measurements for calibrating a PTR-TOF are described,

which are also applicable to PTR-Quad and, with slight changes, to eTR-Quad measurements.

In normal operation, the PTR-TOF mainly measured ambient air, in general over 90% of the time. Three to four times a day, the instrumental background was automatically measured (**paper IV** and **V**) by switching a solenoid three way valve (type 6606 with ETFE, Bürkert GmbH & Co. KG; Fig. 8). In **papers I-III** the background was measured manually and varied in length and frequency, depending on accessibility of the measurement site (e.g. opening hours of the Bosco Fontana nature reserve park; **paper III**).

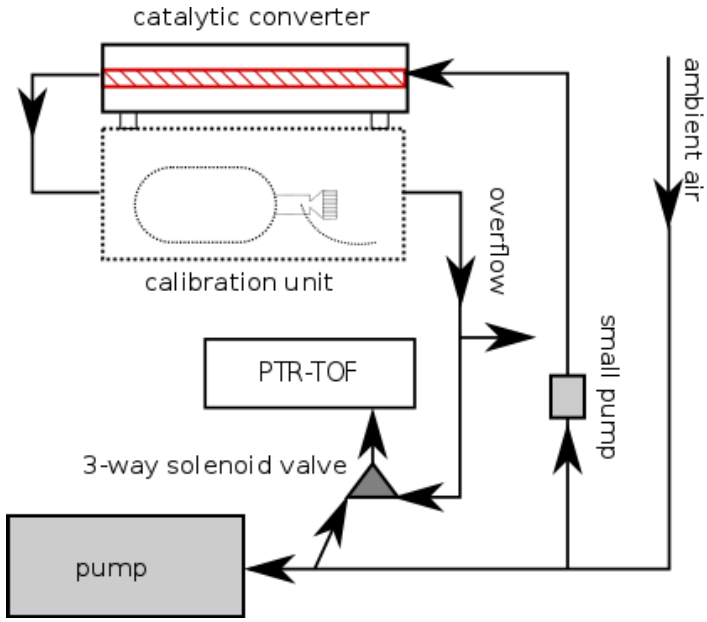

Figure 8: Inlet system for measuring and calibrating the PTR-TOF. The calibration unit is disconnected when the instrument is not being calibrated. Figure adapted from **paper II**.

To measure the instrumental background, a commercial zero air generator (Parker Balzon HPZA-3500-220; **paper I**) and a homemade catalytic converter (**papers II-V**) were used. The custom build catalytic converter consisted of a stainless steel tube, filled with catalytic granulate (EnviCat 2531, Süd-Chemie AG) and heated to 350°C. In operation, ambient air was guided through the converter to create VOC-free air (zero air) with the same relative humidity as in the ambient conditions. Depending on the inlet system and the stickiness of the compounds of interest, different turnover times should be used for measuring the instrumental background. As an example, Fig. 9 shows the time response of methanol, acetone and isoprene. The calibration gas was added shortly after 10:15. The isoprene signal was steady from the beginning, while acetone needed 20 min to stabilize and methanol was not stable after 1 h of measurements. A similar pattern is shown on the right side, where the standard gas was spiked and then constantly added. Also the isoprene signal here is constant right away. Acetone took 25 min and methanol needed the longest to stabilize. Noteworthy, these response times are dependent on the concentration difference, which were over 5 ppb

(for the not spiked part) in Fig. 9. Therefore the response times are much faster when switching from ambient air to zero air. In **papers IV** and **V**, 25 min averaging time for the background measurements were used.

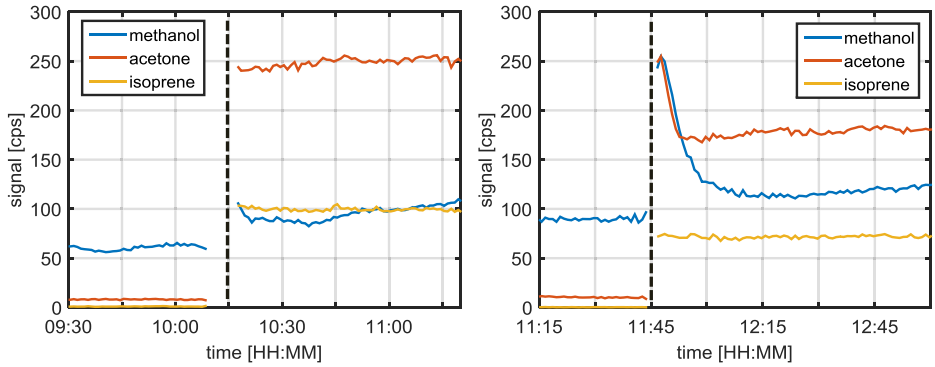

Figure 9: The time response of the instrument and inlet system for different calibration gases. The dashed black line marks the addition of the standard gas.

Every two to three weeks the PTR-TOF was calibrated. A calibration consists of a background measurement followed by measuring a calibration standard, both using the same port of the three way valve (Fig. 8). The calibration standards used in the studies were from Apel Riemer Environmental Inc. and contained a variety of different compounds. The main compounds which were always present in the standard were methanol, acetonitrile, acetaldehyde, acetone, isoprene, methyl ethyl ketone, benzene, toluene, xylene and α-pinene. The concentration in the standard bottle was approximately 1 ppm for each of the 15 to 20 VOCs; therefore, it still needed dilution with zero air to get to concentration levels of around 7 ppb. Similar to the background measurements, the calibration time can be dependent on the material and length of the tubing used in the calibration setup, as well as on the compounds of interest (see Fig. 9).

Amines such as trimethylamine, which was measured and calibrated with a liquid calibration unit in **paper I**, need long times until a stable signal can be recorded. As the surfaces of tubing used in the calibration setup act as a sink, changes to higher and lower concentrations need time to equilibrate. Accordingly, a compromise between calibration time and ambient measurements must be made. From the zero air and the calibration standard measurements, the sensitivities of the calibration compounds can be calculated by fitting the slope of the counts measured at different calibration standard concentrations.

As the primary ion signal could change between zero air measurements and/or calibrations, which would also change the count rate of all measured peaks, all signals are normalized to 10^6 cps primary ions. Therefore, the measured signals are multiplied by 10^6 and divided by the up-scaled signals of the $H_3[^{18}O]^+$ and $H_5O[^{18}O]^+$.

At this point, the concentrations of the measured compounds can be calculated. First, the background signal is linearly interpolated and subtracted from the ambient measurements. This background corrected data is compared to the limit of detection (LOD). In the PTR

community the LOD is commonly defined as two times the standard deviation of the background measurement (Fig. 10). If the signal of a compound is above the limit of detection, its concentration is calculated. For non-calibrated compounds the sensitivity is based on similar compounds or calculated as discussed in Sect. 3.1.

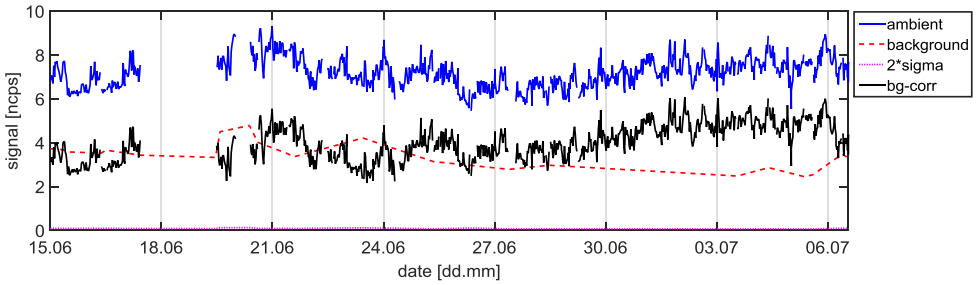

Figure 10: Time trace of acetonitrile (42.0338 Th) during measurements in Bosco Fontana, Italy. The 2*sigma represents the limit of detection and is two times the standard deviation of the background signal. The bg-corr graph corresponds the ambient measurement where the background signal was subtracted.

The GC-MS in **paper IV** was calibrated using adsorbent tubes in which a mixture of liquid standards and MilliQ water was injected. The tubes were then flushed with 80 mL min^{-1} of high purity nitrogen for 10 minutes to remove the water. These samples were desorbed at 300°C and directed to the cold trap in a helium flow and analyzed under similar conditions as the ambient measurements. For more detailed information see **paper IV**.

2.5 Exchange and emission measurements

VOC fluxes describe the net exchange of VOCs between the biosphere and the atmosphere, and therefore, are important to identify sources and sinks of various compounds. The exchange together with transport and air chemistry defines the VOC concentrations in the atmosphere. Depending on the measurement height, wind speed and turbulence, the footprint of the flux measurements can be tens of meters to several kilometers (Horst, 1999). To ensure that the measured flux is representative of the ecosystem, the measurement site must be homogeneous. Flux measurements are made at different scales, from leaf and branch emissions using cuvettes and chambers to measurements that include whole ecosystems by using eddy covariance (EC) and surface layer profile (SLP). In this thesis, mainly the EC method has been used.

Ecosystem exchange: direct methods

Eddy covariance is a direct measurement method for ecosystem exchange (Aubinet et al., 2012; Montgomery, 1948). The measured flux (F) can be described as a covariance between the vertical wind speed fluctuations (w') and concentration fluctuations (c'; Fig. 11):

$$F = \overline{w'c'}, \tag{4}$$

which can be reformulated as:

$$\overline{w'c'} = \frac{1}{n}\sum_{i=1}^{n}(w_i - \bar{w})(c_i - \bar{c}), \tag{5}$$

where $w_i$and c_i are the individual measurement points, $\bar{w}$ and $\bar{c}$ are the mean values, i the number of the individual measurement and n the total number of measurements. Figure 11 visualizes the outcome of the necessary calculations (Eq. 5) for calculating the flux.

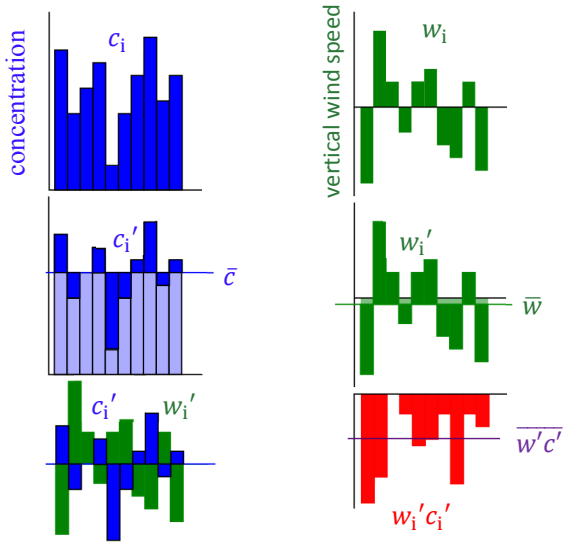

Figure 11: Visualization of the flux calculation process.

As the vertical wind speed fluctuates at a high frequency, both the wind and concentration measurements must be recorded with high time resolution. Fast measurements of wind speed are possible by using 3d-anemometers, which use ultrasonic sound waves to measure wind speed with up to 100 Hz. Fast VOC concentration measurements are more problematic to acquire, as only the TOF mass selectors are capable of recording hundreds of different VOCs in a sub second time resolution. The PTR-TOF in **papers II, III** and **V** was acquiring data with a 10 Hz frequency.

The Eqs. 4 and 5 assume that the wind and VOC concentrations are recorded at the same time. This is not the case as the PTR-TOF needs an air conditioned housing and has to sample VOCs through an inlet, while the wind measurements are instantaneous. Especially when measuring from a tower and/or above canopy, the VOC concentration lag behind the wind measurements. This lag time is caused by the time the VOCs need to pass through the inlet and the response time of the instrument itself. Often the data of the vertical wind and VOC concentrations are recorded by different computers which do not have the exact same time and can also shift during measurements. The correction for this depends on the measurement setup. If the wind and the concentration data are collected on the same computer, the lag time can be very stable. This was the case in **papers II** and **III** where the lag time

for the whole campaign was 2.6 s. On the other hand, in **paper V** the two data sets were recorded with different computers and the lag time had a continuous shift as well as abrupt jumps. The lag time varied between zero and 50 seconds.

The calculation of the correct lag time (λ) starts with calculating the cross covariance function (CCF). The cross covariance function is calculated by using Eq. 5, w_i and c_{i-x}, where x is varied between -2000 and +2000. This results in a shift between c and w, which changes the calculated flux ($\overline{w'c'}$). In Fig 11 an x of 5 would correspond to a shift of the blue dataset (bottom left panel) 5 steps to the left, before the flux is calculated. The variation of x also reduces the number of data points from n to n-x. The maximum of the CCF defines the lag time λ, which is used for the calculation of the final flux value. The lag time is defined as follows

$$\lambda = x \cdot \Delta t, \tag{6}$$

where x is the lag in data points and Δt is the time resolution of the measurements. A 30 minute CCF of monoterpenes, measured in Hyytiälä, is shown in Fig. 12. As the calculated fluxes a low, instrumental noise heavily affects the position of the maxima, leading to overestimations of the flux. Therefore, the maximum of the smoothed (running mean) CCF determined the lag time (Taipale et al., 2010; Langford et al., 2015). The actual flux value was then taken from the original CCF (unsmoothed).

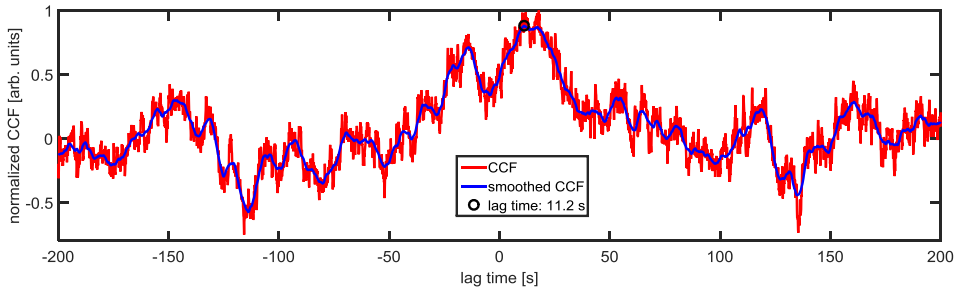

Figure 12: A cross covariance function (CCF) of monoterpenes from the 21.04.2013 15:15 recorded in Hyytiälä.

Another type of eddy covariance flux measurements is the virtual disjunct eddy covariance (vDEC) described in Karl et al. (2002) and used in **paper III**. It is similar to the EC method, although it uses fewer measurement points and is, therefore, usable for the PTR-Quad. A typical time resolution when using vDEC is 2 Hz, which leads to a total of 3600 data points per 30 min measurement interval. If ten compounds are measured, each compound will have 360 data points. This is the major difference from the EC method, where each compound would have 18000 data points. Therefore, the standard deviation (= statistical uncertainty) in vDEC is larger by a factor of seven ($\sqrt{18000/360}$), if compared to EC.

Ecosystem exchange: Indirect methods

For instruments which have a lower time resolution than 1 Hz (e.g. GC-MS), ecosystem fluxes can be measured by using the surface layer gradient or surface layer profile (SLP)

method (Rannik, 1998; Rantala et al., 2014). The gradient method uses concentration measurements from two measurement heights, while the profile method uses more than two different heights. The use of more heights lowers the statistical error and reduces chances for systematic errors.

In contrary to the EC or vDEC, the gradient method is indirect meaning that the turbulence in not measured and is, therefore, described by a calculated stability parameter:

$$F_{\text{gradient}} = -K\frac{\partial \bar{c}}{\partial z}, \tag{7}$$

where $\frac{\partial \bar{c}}{\partial z}$ is the vertical gradient of the VOC concentration and K is the turbulent transfer coefficient (Rantala et al., 2014). Indirect methods have been proven to work well in low flux ecosystems with stable nights, as is the case at the SMEAR II station in Hyytiälä (Rannik et al., 2004; Rantala et al., 2014 and 2015). These methods are especially useful for instruments with lower time resolution such as the PTR-Quad.

Emission from enclosures

Emission measurements of leaves or small samples can be measured with enclosures. In **paper I** a 41 L dynamic chamber (Pape et al., 2009) was used to measure emissions from different cow excrements to identify the source of different VOCs, ammonia and trimethylamine (TMA). The emission (E_{cham}) of the perfluoroalkoxy alkane-coated chamber can be calculated as:

$$E_{\text{cham}} = \frac{Q}{A} \cdot \rho_{\text{d}}(c_{\text{cham}} - c_{\text{amb}}), \tag{8}$$

where Q is the volumetric flowrate through the chamber, A is the surface area of the sample, ρ_{d} is the dry air density and c_{cham} and c_{amb} are the concentrations of the air after and before passing through the chamber, respectively. To have comparable results, the relative humidity was kept constant at 60% and temperature at 20°C.

In **paper III**, a flat 6 cm^2 leaf cuvette system (LI6400, Li-COR) was used to characterize leaf emissions. The VOCs were collected under standard conditions of 30°C, 1000 µmol m^{-2} s^{-1} photosynthetically active radiation (PAR) and 400 ppm CO_2 and were trapped in Tenax tubes. The samples were stored at 4°C until they were analyzed by the GC-MS.

3 Challenges in measuring VOC concentrations

3.1 PTR sensitivity

For the calculation of the sensitivities of the most abundant VOCs, standard gas mixtures are used. These VOCs, such as isoprene, α-pinene, methanol, acetone, benzene and toluene, can be calibrated as described in Sect. 2.4. Data from calibrated compounds are very robust as, when calibrated under similar conditions to ambient measurements, many possible error sources, e.g. fragmentation, are corrected for.

Often compounds not included in a calibration standard are important to the ecosystem or a scientific question. When a custom calibration gas or a liquid calibration is not available, too expensive or delivery times are too long, one of the following methods can be used to get to useful sensitivities.

Deriving bulk sensitivities

One method to estimate the sensitivities is by using a bulk sensitivity of a similar compound group (Tab. 3). In **papers II** and **V** the calibrated compounds have been assigned to pure hydrocarbon, oxygenated, and nitrogen containing groups. All of the sensitivities inside one group are averaged and used for all uncalibrated compounds of the same group. If this approach is used, all data have to be duty cycle corrected, otherwise lighter compounds would be underestimated and heavier compounds would be overestimated. For this method no additional calculations or calibrations are needed, and the method is based on measured sensitivities; however, this method does not take possible fragmentation into account.

Table 3: Compound specific sensitivities of the three calibrations during the Bosco Fontana campaign. The calculated bulk sensitivities for non-calibrated compounds are in the last row.

mass [Da]	compound	elemental composition	10.06.2013 [ncps/ppb]	22.06.2013 [ncps/ppb]	11.07.2013 [ncps/ppb]
42.0338	acetonitrile	$C_2H_4N^+$	19.6	17.5	17.3
45.0335	acetaldehyde	$C_2H_5O^+$	-	-	19.0
57.0335	acrolein	$C_3H_5O^+$	-	-	16.6
59.0491	acetone	$C_3H_7O^+$	20.3	18.5	20.3
69.0699	isoprene	$C_5H_9^+$	11.2	10.5	10.7
73.0648	butanone	$C_4H_9O^+$	20.7	18.3	19.2
79.0542	benzene	$C_6H_7^+$	11.4	10.7	12.0
81.0699	a-pinene-fragment*	$C_6H_9^+$	7.3*	7.0*	6.2*
93.0699	toluene	$C_7H_9^+$	14.1	13.4	13.0
107.0855	o-xylene	$C_8H_{11}^+$	15.0	14.3	13.1
121.1012	trimethylbenzene	$C_9H_{13}^+$	14.7	14.1	-
129.0699	naphthalene	$C_{10}H_9^+$	14.3	10.2	-
137.1325	α-pinene*	$C_{10}H_{17}$+	8.2*	7.9*	6.9*
CH	13.0 ncps/ppb	CHO	19.1 ncps/ppb	CHN	18.1 ncps/ppb

(*) the sensitivities of α-pinene and its fragment were summed up to calculate the bulk sensitivity.

Calculated sensitivities

Sensitivities can also be calculated using a more theoretical approach, which uses the reaction rates (k_{ado}). These reaction rates (Eq. 1) can be calculated following Su & Chesnavich et al, (1982) for polar or the Langevin approach for non-polar compounds (e.g. Zhao and Zhang, 2004):

$$k_{\mathrm{ado}} = \left(\frac{2\pi q}{\sqrt{\mu}}\right)\left[\sqrt{\alpha} + C\mu_{\mathrm{D}}\sqrt{\frac{2}{\pi\, k_B\, T}}\right] \tag{9}$$

In this equation q describes the electric charge, μ is the reduced mass of the reactants, α is the polarizability, μ_D is the permanent dipole moment, T is the temperature and k_B is the Boltzmann constant. C is a parametrized value between 0 (in case of a non-polar compound) and 1 (for polar compounds), and can be described as a function of permanent dipole moment and polarizability $C = f\left(\frac{\mu_{\mathrm{D}}}{\sqrt{\alpha}}\right)$.

The concentration of a compound $[VOC]$ can be then calculated as:

$$[VOC] = \frac{c}{k_{\mathrm{ado}}\, t}[VOC \cdot H^+]\,, \tag{10}$$

where t is the reaction time, $[VOC \cdot H^+]$ is the measured signal on the protonated mass of the compound of interest and c includes the transmission (duty cycle) and primary ion correction (not used, if the measured signal has already been corrected for primary ions). This method is used to calculate the transmission curve for the PTR-Quads from the calibrated sensitivities (Taipale et al., 2008). In **papers III** and **V** this transmission curve was used to estimate the sensitivity of non-calibrated compounds measured by PTR-Quad.

A recent study, using a PTR-TOF showed less than 10% discrepancy when comparing theoretical and experimental reaction rates (Cappellin et al., 2012). However, this comparison was made in laboratory conditions with the knowledge of the compounds and respective fragmentation patterns (see Sect. 3.2).

Duty cycle correction

When using estimated or calculated sensitivities, each compound has to be corrected for the mass dependent duty cycle in the PTR-TOF (Chernushevich et al., 2001):

$$\text{duty cycle } ({}^{m}/_{Z}) = \frac{\Delta l}{D} \cdot \sqrt{\frac{{}^{m}/_{Z}}{{}^{m}/_{Z_{\mathrm{max}}}}}, \tag{11}$$

where Δl is the length of the extractor (Fig. 5), D is the distance between the center of the extractor and the center of the detector, ${}^{m}/_{Z}$ is the mass to charge ratio of the compound of interest and ${}^{m}/_{Z_{\mathrm{max}}}$ is the last (=heaviest) bin measured. The unit-less factor $\frac{\Delta l}{D}$ is 0.29 in the used TOF (H-TOF, Tofwerk AG) and it explains how much of the heaviest ions are lost

due to the geometry of the instrument. The $\sqrt{\frac{m/z}{m/z_{max}}}$ describes the loss of small, faster ions, while the instrument is waiting until the heaviest, slowest ions reach the detector.

3.2 Problems with fragmentation

Even though PTR-MS is known as a soft and sensitive ionization method (Lindiger et al., 1998; Hansel et al., 1999), still many compounds fragment (e.g. Gueneron et al., 2015). If the fragmenting compound is calibrated and the fragmentation pattern is known, then it can be easily corrected. If the compound is not calibrated, the fragmentation leads to a signal shift from the parent ion to the fragment, complicating the interpretation of the measured spectra and the identification of the sources. Especially when the majority of the measured signal is on the fragment and fluxes or concentration are low, it is difficult to identify the parent masses. In order to resolve fragmentation, the signal of the fragmenting compound as well as its fragmentation pattern must be known. Major compounds which could be affected by fragmentation include:

MBO (2-methyl-3-buten-2-ol; $C_5H_{11}O^+$) is well-known to lose an H_2O molecule during the protonation (Fall et al., 2001; de Gouw and Warneke, 2006; Kaser et al., 2013) and then become undistinguishable from isoprene, which is not known to fragment easily. In **papers II** and **III** MBO was disregarded as a major influence, since the main tree species are not known to emit it, which was confirmed by the leaf cuvette measurements. Furthermore, no flux on the parent mass of MBO was discovered, which also excludes the understory of the forest in Bosco Fontana as a major source of MBO. In Hyytiälä, however, fluxes of MBO have been measured several times (Tarvainen et al., 2005; Hakola et al., 2006; Rantala et al., 2015), and therefore it was suspected in **paper V** that the isoprene signal was influenced by MBO. However, no fluxes could be seen on the parent mass of MBO with the PTR-TOF. This can be explained by its fragmentation pattern, where only less than 25% (Kaser et al., 2013) are measured on the parental mass, leading to a flux under the detection limit. To measure the MBO signal without the fragmentation, an eTR-MS could be used, but so far no measurements with O_2^+ as the primary ion have been made in Hyytiälä.

Similar to MBO and many other alcohols, butanol can also lose a water molecule during the protonation process (Spanel and Smith, 1997; Denzer et al., 2014) and fragment into butene. The identification of the sources of butene are challenging, as it is emitted by vegetation (Goldstein et al., 1996; Hakola et al., 1998) and from anthropogenic sources (Harley et al., 1992; Na et al., 2004). Furthermore, the butene signal has the same nominal mass as a water cluster isotope ($H_7O_2[^{18}O]^+$), which cannot be distinguished with a PTR-Quad and can disturb the ambient butene flux measurements. In Hyytiälä, the butene fluxes came exactly from the directions where the aerosol instrumentation was measuring (**paper V**), therefore, we concluded that the measured butene was the fragment of butanol.

The toluene signal can also be affected by the fragment of para-cymene (Tani et al., 2003). At the instrumental settings used in **paper V**, over 75% of the p-cymene should fragment to the toluene signal.

Acetic acid was measured in **papers II-V** and is known to fragment to $C_2H_4O^+$ when using the PTR method (Baasandorj et al., 2015). Therefore, the sensitivity was approximated by half of the bulk sensitivity (Sect. 3.1) in **paper II** and half of the acetone sensitivity in **paper IV**.

3.3 Losses in the sampling system

Another source of uncertainty in the concentration measurements is the loss rate of various compounds in the inlet and inside the PTR-TOF. Depending on the stickiness of the measured VOCs, the sample flow, the sampling system material and the inlet length can influence the measurements drastically. One key parameter is the turnover time of the instrument, which describes the relation between sample flow and the volume of a system.

In **papers I** to **V** of this work, the various ambient inlet systems were not calibrated, as an independent calibration setup was used (Sect. 2.4). This improves the time response of the calibrated compounds and makes a quick standard measurement possible and thereby maximizes the time for ambient measurements. For most of the compounds, minimal to no inlet losses are expected as the residence time was less than 3 s in **papers I** to **IV** and under 8 s in **paper V**. To also characterize the inlet losses, an individual high flow calibration system would be needed, which can create zero air with a rate of up to almost 100 L min^{-1}. For very sticky compounds a second identical inlet line would be needed, so that compounds lost on the line surfaces during calibrations are not influencing the ambient measurements.

In **paper I** the line losses were anticipated, as amines and ammonia tend to be easily lost to walls of the tubing (Mikoviny et al., 2010). The inlet used in this campaign could not be shortened since a degree of flexibility was needed to follow the moving cows in the yard of the farm. Therefore, the inlet line was heated to above 150°C and flushed with a flow rate of 80 L min^{-1} in order to minimize the response time and surface displacement issues.

In **paper IV** the acetic acid concentrations were measured with GC-MS and the PTR-TOF. The two instruments showed a significant difference in the volume mixing ratios. The inlets of the two instruments were similar. The PTR-TOF used a 3.5 m long, 4 mm i.d. (inner diameter) polytetrafluoroethylene (PTFE) line with a 20 L min^{-1} flow. The GC-MS used a 3 m long fluorinated ethylene propylene (FEP) inlet with 3.2 mm i.d. which had a flow of 2.2 L min^{-1}. As already mentioned in Sect. 3.2, acetic acid fragments when protonated. However, even when taking this into account, the PTR-TOF still showed much smaller concentrations than the GS-MS. When comparing the ambient signal with the background signal (Fig. 13), it was seen that the two signals followed the same pattern. If the PTFE and FEP have similar surface loss rates, the inlets themselves should be comparable and not cause a big discrepancy. The difference is most likely caused by a memory effect between

the three way valve and the instrument itself (Fig. 8). Memory effects of acetic acid in PTR measurements have been reported by de Gouw et al. (2003).

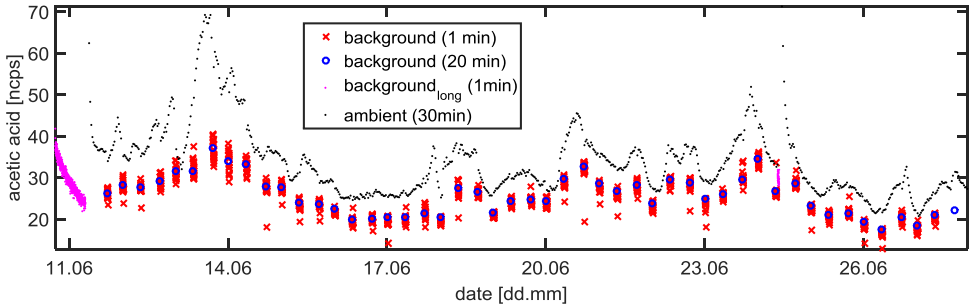

Figure 13: Ambient and background measurements of acetic acid in Hyytiälä.

4 Insights into VOC exchange

4.1 Ecosystem exchange

In this thesis three different methods for measuring ecosystem exchange are compared: EC, vDEC and SLP (Table 4). In **paper III** the fluxes of monoterpenes and isoprene are compared for the vDEC (PTR-Quad) and EC (PTR-TOF). As discussed in Sect. 2.5, these two methods are very similar with the difference being the number of data points used for the flux calculation. The isoprene fluxes correlated very well with an R^2 of 0.91, which can be explained by the clear emissions, which were coming from the oak-hornbeam forest. Also $C_5H_9^+$ (69.0699 Th) was the only peak at nominal mass 69 Da, and, therefore, the high resolution signal from the PTR-TOF should match the nominal resolution data from the PTR-Quad. Still, the mean flux differed by a 32% or 1.88 nmol m^{-2} s^{-1}. As the instruments were sampling from the same inlet line and used the same 3d-anemometer data, this discrepancy probably arises from uncertainties of the sensitivity or differences in the data analysis.

The second comparison was between the monoterpenes ($C_{10}H_{17}^+$, 137.1325 Th) measured at their main fragment $C_6H_9^+$ (81.0699 Th). Here, the monoterpene fragment was used, as the PTR-Quad had transmission problems at higher masses (**paper III**). The exchange measured by the two mass spectrometers correlated with an R^2 of 0.50. The mean monoterpene flux of 0.12 nmol m^{-2} s^{-1} (7.2 10^9 cm^{-2} s^{-1}; vDEC) was 32% smaller than the 0.18 nmol m^{-2} s^{-1} measured by EC. The poor correlation for monoterpenes can be explained by the low fluxes, which were more influenced by noise than the isoprene fluxes. Especially for PTR-Quad, which had a low sensitivity at this mass, higher scatter was observed. Due to technical problems, the PTR-Quad sensitivity was so low during the second half of the campaign, that no monoterpene vDEC flux could be measured. Another source of discrepancy was that three additional peaks at nominal mass of 81 Da were seen by the PTR-TOF. Therefore, the EC flux was just calculated from the signal from the monoterpene fragment, while the PTR-Quad calculated the fluxes from the summed up signal of the four mass peaks.

In **paper V** a comparison between eight compounds measured by EC with a PTR-TOF and SLP used by a PTR-Quad was made. Compared to the previous comparison in **paper III**, the results were expected to differ more, as they were obtained by methods that differ in various ways, e.g. measurements were performed 25 m apart and were using different inlets. As the SLP fluxes were calculated from 16.8 m, 33.6 m, 50.4 m and 67.2 m, the calculated measurement height was 36 m, compared to the 23 m for the EC fluxes, leading to different footprint areas. The fluxes of methanol, acetone and the monoterpenes agreed within 20%, and had the highest data coverage for the comparison: 92, 119 and 116 data points, respectively. These three compounds all have fluxes above 0.150 nmol m^{-2} s^{-1}, and no major fragments influence their signal. The best correlation between EC and SLP fluxes was observed for methanol and the monoterpenes, with an R^2 of about 0.35. The methanol sensitivity for

the PTR-Quad was estimated from the transmission curve, therefore the disagreement of the mean flux is higher than for the monoterpenes and acetone.

For compounds with smaller fluxes, like acetonitrile and acetaldehyde, the methods agreed within 70%, although the comparison here is based only on 55 and 49 data points, respectively. The amount of data points in combination with the low signal makes the fluxes of the two compounds prone to measurement uncertainties.

Acetic acid, isoprene and toluene had much smaller fluxes with the EC method when compared to the SLP method. One reason could be that acetic acid, isoprene and toluene are influenced by fragmentation (Sect. 3.2), which is backed up by the differences in the measured concentrations at least for toluene and acetic acid. The huge discrepancies in the acetic acid fluxes are amplified by the memory effect, which we see with the PTR-TOF (Sect 3.3).

Table 4: Comparison between the EC and vDEC fluxes measured in Bosco Fontana and the EC and SLP method used in Hyytiälä.

campaign	compound	measured elemental comp.	mean flux (PTR-Quad) [nmol m^{-2} s^{-1}]	mean flux (PTR-TOF) [nmol m^{-2} s^{-1}]	Δ flux [%]	R^2
Bosco Fontana	isoprene	$C_5H_9^+$	4.10 (vDEC)	5.98	32	0.91
Bosco Fontana	monoterpenes*	$C_6H_9^+$	0.12 (vDEC)	0.18	32	0.50
Hyytiälä	methanol	$C_1H_5O^+$	0.447 (SLP)	0.553	19	0.37
Hyytiälä	acetone	$C_3H_7O^+$	0.176 (SLP)	0.173	2	0.05
Hyytiälä	monoterpenes	$C_{10}H_{17}^+$	0.282 (SLP)	0.261	8	0.36
Hyytiälä	acetonitrile	$C_2H_4N^+$	-0.009 (SLP)	-0.017	47	<0.01
Hyytiälä	acetaldehyde	$C_2H_5O^+$	0.019 (SLP)	0.063	70	0.03
Hyytiälä	acetic acid	$C_2H_5O_2^+$	0.336 (SLP)	0.025	1244	0.06
Hyytiälä	isoprene	$C_5H_9^+$	0.082 (SLP)	0.035	134	0.12
Hyytiälä	toluene	$C_7H_9^+$	0.138 (SLP)	0.027	411	0.09

* the monoterpene flux was calculated from the monoterpene fragment ($C_6H_9^+$)

Overall, the major compounds agree reasonably well, but special care must be taken when working with small fluxes or fluxes of compounds, which are influenced by fragmentation as their uncertainties increase drastically (Table 4).

4.2 Challenges in the upscaling of emission

Paper III connected the above canopy flux of isoprene and monoterpenes, measured by vDEC, and leaf level emissions recorded with the GC-MS. To upscale the leaf level emissions, a detailed map of the plant cover inside Bosco Fontana is needed. Dalponte et al. (2007) published the tree species distribution inside the natural reserve using lidar data. This map had a resolution of 5 m^2 and contained the fraction of twenty different tree species in each grid cell. A 2-dimensional footprint model (Kormann and Meixner, 2001) was then used to identify which grid cells were in the footprint of each individual 25 min flux and how much each species contributed to this ecosystem flux. The emission rates of the leaf

cuvette measurements were then calculated for each of the species. The leaf level measurements in Bosco Fontana covered over 75% of the species, and literature values were used for the missing species (see **paper III**). Literature values using emission rates in $\mu g\ g_{DW}^{-1}\ h^{-1}$ (DW=dry weight) were converted to mg $m^{-2}\ h^{-1}$ by using the factor of 115 $g_{DW}\ m^{-2}$. The emission rates were then scaled up using the MEGAN algorithm (Guenther et al., 2006), as well as the measured temperature and PAR data. For the single sided leaf area index, a value of 5.5 was used.

The upscaled fluxes of monoterpene and isoprene underestimated (<60%) the flux when compared to the measured ecosystem flux, and in the case of isoprene, the upscaled flux described the variations better than the modeled ecosystem flux. The underestimation of the flux could have various reasons. One is a change in the plant distributions since 2007. This could affect the undergrowth, although the tree distribution should not change in five years by natural processes. A man made change happened during 2007 and 2012, a non-native species (*Quercus rubra*) was gradually removed from the forest. However, this should have decreased the isoprene flux, as this species is an isoprene emitter (Harley et al., 1999). Therefore, it cannot be the cause of the isoprene underestimation of the upscaled flux. Other sources for the missing flux could be the undergrowth, stem and soil emissions; however, as just limited amount of light reaches the forest ground, these emissions were considered negligible and not further researched. The reason for the low bottom-up isoprene flux is probably that the emissions from the leave cuvette were measured from the ground level and thereby not representative of the emissions from the canopy top, where most radiation is absorbed and highest emissions occur. Using literature values (Karl et al., 2009) for the two most common isoprene emitters in the forest increased the bottom-up flux by 130%, and improved the correlation further. Overall, an important question is how representative a onetime emission measurement of one leaf is when upscaling it to ecosystem fluxes. Genard-Zielinski et al. (2015) measured isoprene emissions of different *Quercus pubescens* trees from the same forest, and the variation of the standardized emissions varied considerably.

The arguments from above also apply for the monoterpene flux upscaling. Bertin et al. (1997) observed, that the monoterpene emission potential of sun-exposed and shade-adapted branches of *Quercus ilex* varied with up to 190%. Additionally, as monoterpenes can be very reactive, the chemical loss between the emission and the detection by instrument have to be considered. In **paper II** the chemical loss for α-pinene is estimated to be within 5% to 20% range.

In Fig. 14 the measured and calculated upscaled fluxes of isoprene and monoterpenes during the 02.07.2012 are shown. For the isoprene flux, the upscaling showed a slight underestimation before noon and an overestimation around 15:00. The isoprene flux was dominated by *Quercus robur* and *Quercus rubra* until the wind direction changed and *Populus x canescens* contributed to the emissions. As expected, the isoprene emissions followed the PAR well, as isoprene is directly emitted when created from biosynthesis.

The monoterpenes were mainly emitted by *Carpinus betulus* and were approximately a factor of 10 smaller than the isoprene emissions. The upscaled flux was underestimating the measured fluxes for most of the day, especially at 11:00 and during the night. The main trend of the emissions is also captured by the upscaled leaf emissions.

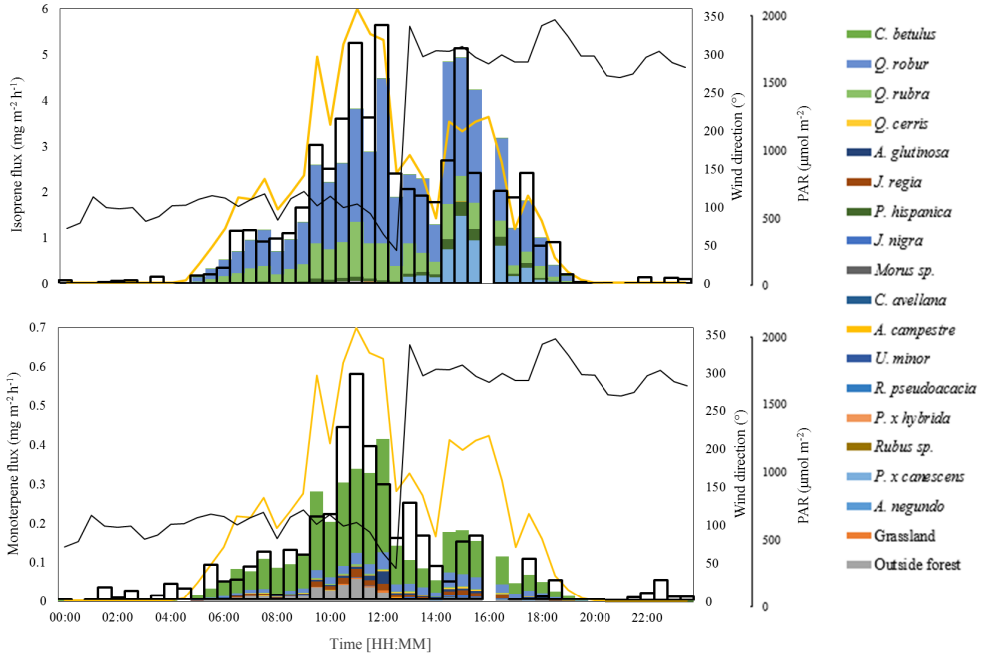

Figure 14: Measured vDEC fluxes (black bars) of isoprene and the monoterpenes at the 02.07.2012. The upscaled fluxes are the colored bars (colored by source). The wind direction (black line) and PAR (orange line) are also shown. This figure is adapted from **paper III**.

4.3 Improvements to the compound flux detection

One of the advantages of the PTR-TOF is that it measures all VOCs above the limit of detection simultaneously. This can, however, become a burden, if very work intensive tasks have to be made for hundreds of masses. This was the case in the classification of the VOCs with exchange. The method was already used with PTR-Quads and consisted of manually checking the cross covariance functions (Fig. 15A; Sect. 2.5). This task was still manageable with around ten compounds when using vDEC; however, with several hundreds of mass peaks, this requires to a manual check of thousands of cross covariance functions.

In **paper II** this method was called the manual method. It is time consuming and the classification, whether a certain CCF maximum is clearly above the surrounding noise or not, is subjective. Therefore, an automated method, developed by Park et al. (2013) and used in

paper II was tested. This method calculates an average and absolute maximum (Fig. 15B and 15C), and compares these values to different noise thresholds. Taking the absolute of the CCF ensures that emissions and depositions do not cancel each other out when averaged. However, taking the absolute value also lowers the σ_{Noise}, as can be seen in Figs. 15A and 15B. The mean noise in the original CCF is 4% of the maxima and the 3 σ_{Noise} 62%. In case of the absolute CCF the 3 σ_{Noise} variation of the data is less, 39%, as the signal just varies between 0 and 100%, and not like previously from -100% to 100%. This makes a comparison between higher sigma thresholds of absolute and original CCFs difficult. However, the mean noise corrects for this discrepancy as it increases for the absolute CCF (18%). In Bosco Fontana, the averaged, absolute CCF thresholds for 10 σ_{Noise} were higher than the 10 σ_{Noise} thresholds of the original CCF for the same period.

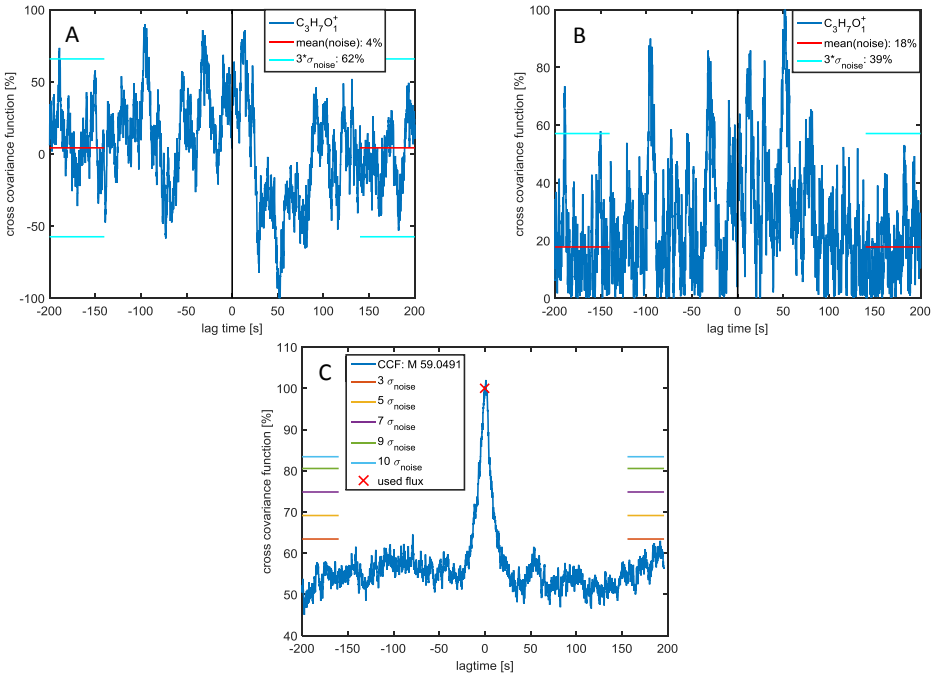

Figure 15: Cross covariance functions (CCF) for acetone. Panels A and B are for one 30 min averaged CCF and show an original CCF (A) and an absolute CCF (B). Panel C shows the mean averaged CCF, which uses data from all CCFs between 10:00 and 16:00, together 203 30 minute CCFs. This figure is adapted from **paper II**.

The used time window should reflect periods with high turbulence, which occur when the sun is shining and heating the canopy or the forest floor. In **papers II** and **V** this time window was from 10:00 to 16:00 (CET for Bosco Fontana, CET+1 for Hyytiälä). The threshold value was chosen to be $3\sigma_{Noise}$, the standard variation from the borders of the CCF function. The selection of the period influences which compounds pass the threshold. This can be seen in Table 5 where the first nine days and the first 21 days of June were searched for

VOCs with exchange. In total 13 masses passed the 3 σ_{Noise} threshold in only one of the two characterizations.

The automated method found more compounds with flux. This can be explained by the usage of the averaged CCF, which reduced the σ_{Noise} by a factor of $\frac{1}{\sqrt{N}}$, N being the number of averaged 30 min files. In **paper II** N was 203 and in **paper V** N was 243 for 21 days and 142 for 9 days. The amount of data depends on the occurrence of background measurements, calibrations or technical problems with the instrument. In Bosco Fontana, the manual method found five compounds with exchange, while the automated method discovered 29. The additional 24 compounds increased the downward flux by a factor of two and the upward flux by 122%. Using the automated method added 1.6 nmol m^{-2} s^{-1} to the net flux, although the classical method still captured over 80% of the net flux.

Table 5: All masses (including background masses, bg) that passed the threshold 3 $\boldsymbol{\sigma_{Noise}}$ during the classification for 9 days or 21 days in June. $\left(\frac{M}{\sigma_{Noise}}\right)$ is the ratio between the maximum of the mean, absolute CCF (M) and the $\boldsymbol{\sigma_{Noise}}$. Not identified compounds are marked with n.i, fragments are labelled with –frag and water cluster signals with w.c.

mass [Da]	$\left(\frac{M}{\sigma_{Noise}}\right)_{9d}$	$\left(\frac{M}{\sigma_{Noise}}\right)_{21d}$	compound	mass [Da]	$\left(\frac{M}{\sigma_{Noise}}\right)_{9d}$	$\left(\frac{M}{\sigma_{Noise}}\right)_{21d}$	compound
29.0134	20.0	19.2	HN_2^+ (bg)	60.0471	3.6	3.4	n.i.
31.0178	3.1	1.6	formaldehyde	61.0284	7.2	4.7	acetic acid
32.9971	4.8	6.4	HO_2^+ (bg)	67.0542	4.6	3.5	cyclopentadiene
33.0335	40.1	45.9	methanol	69.0352	8.6	5.8	n.i.
35.0366	6.0	5.2	H_5NO^+ (bg)	69.0699	25.0	23.8	isoprene
36.0430	21.9	19.7	n.i. (bg)	70.0696	3.4	3.1	n.i.
37.0284	1.6	5.3	$H_5O_2^+$ (bg)	73.0495	4.8	2.3	$H_9O_4^+$ (bg)
38.0337	17.9	16.9	n.i. (bg)	81.0335	19.1	16.1	$C_5H_5O^+$ (bg)
41.0386	5.6	4.6	CH- frag.	81.0699	82.9	80.1	monoterp.-frag.
42.0338	2.4	3.1	acetonitrile	84.9500	3.5	2.8	n.i.
43.0178	6.9	6.1	CHO-frag.	89.0386	1.4	3.7	$C_7H_5^+$
44.9971	3.8	5.2	CHO_2^+ (bg)	93.0699	9.2	10.5	toluene
45.0335	8.1	6.0	acetaldehyde	95.0491	3.0	1.2	phenol
47.0200	13.6	12.8	n.i. (bg)	99.0201	3.6	1.9	n.i.
51.0077	1.7	3.5	$H_2O_3^+$ (bg)	99.0769	1.6	3.1	n.i.
51.0441	18.4	17.1	methanol w.c.	135.1168	4.6	1.6	para-cymene
55.0390	83.1	164.6	$H_7O_3^+$ (bg)	137.1325	81.2	59.4	monoterpenes
57.0699	25.4	28.6	butene	145.9745	4.1	1.0	n.i.
59.0491	27.0	28.2	acetone	160.9916	1.1	3.3	n.i.

Overall, the automated method is a fast and objective way to search for compounds with exchange, and the use of this method is recommended.

4.4 Chemistry affecting fluxes

The ecosystem fluxes describe the VOC exchange between biosphere and the atmosphere. The VOC fluxes are observed at the measurement height, where the inlet starts and the 3d-anemomether is positioned. This height influences how much time the VOCs spend in the layer between emission and being measured by the instrument. For compounds with a long

chemical lifetime, this transport time plays a minor role. Faster reacting compounds will, to a certain degree, already be oxidized when reaching the measurement height or instrument (Rinne et al., 2012). This process has two effects, one being the underestimation of the emissions of the emitted compound. The second effect is a wrong attribution to emissions for the oxidation products. Besides transport time and chemical lifetime, the amount of chemical losses depends also on the concentrations of the oxidants, mainly ozone (O_3), the hydroxyl radical (OH) and nitrate radical (NO_3). While measurements of O_3 were available at both measurement stations, NO_3 was calculated by using the concentration measurements of NO_2 and O_3 (Peräkylä et al., 2014). Measuring OH is challenging, as it is either measured indirectly or by laser-induced fluorescence (Mount and Eisele, 1992, and references therein). As none of these instruments were available in Bosco Fontana, an OH proxy calculation was used in **paper II**, which uses the UVB radiation as input parameter (Petäjä et al., 2009):

$$[OH]_{\text{proxy}} = 5.62 \cdot 10^5 \cdot \text{UVB}^{0.62} \quad (12)$$

In the Bosco Fontana studies (**papers II and III**), the ratio between the flux at the measurement height (F) and the true surface exchange (E) was calculated by a stochastic Lagrangian transport model (Rinne et al., 2012). The monoterpenes had the lowest F/E ratio, which was between 0.8 to 0.95, meaning that up to 20% of the monoterpene flux were lost due to oxidation, and therefore, the measured exchange was underestimated.
Isoprene was another compound with chemical losses during the transport time. Here, the F/E ratio was not very high, and only between 3% and 5% of isoprene was oxidized. Due to the huge isoprene emission, however, the effect on the flux of the oxidation products methyl vinyl ketone (MVK) and methacrolein (MACR) was estimated at up to 30% of the measured exchange.

Rinne et al. (2012) calculated the transport loss from a canopy source to the measurement height for Hyytiälä. It showed minimal losses for isoprene through the whole day, while α-pinene losses were around 10% during night (21:00 to 04:00). This is applicable to the monoterpene fluxes measured in **paper V**. Rinne et al. (2012) further calculated the F/E ratio of beta-caryophyllene with 40% to 50%. Similar losses could be one reason for the absence of sesquiterpene fluxes as seen in **paper V**.

Overall, already minor oxidation of large VOC fluxes can boost fluxes of oxidation products as seen in **paper II**. Furthermore compounds with low atmospheric lifetimes can react before reaching the instrument and therefore their exchange under the limit of detection.

4.5 Deposition of methanol

In various ecosystems, such as in SMEAR II, methanol is the most exchanged compound (in units of nmol m^{-2} s^{-1}; **paper V**). Its diurnal behavior with a clear deposition in the early

morning hours and clear emissions in during the day is very interesting. The dynamic behavior of methanol shows how VOCs are emitted or deposited depending on several meteorological and environmental factors. It also shows the necessity of measuring exchange, as, e.g., with dynamic chambers a separation between natural deposition and losses on the chamber walls is very complicated (Aalto, 2015).

In Fig. 16 the diurnal cycles of the methanol flux from Hyytiälä (**paper V**) and Bosco Fontana (**paper II**) are shown. The deposition of methanol started at both sites at 02:00 (local wintertime for both places) and while in Hyytiälä deposition stopped at 06:00, in Bosco Fontana the deposition lasted until 08:00.

The major chemical sink for methanol are reactions with the OH radical (Heikes et al., 2002). Chemical lifetimes are on the order of ten days, e.g. 11 days (Jacob et al., 2005) or 18 days (Heikes et al., 2002). As OH concentrations are highest during daytime, the chemical sink cannot be the main reason for the methanol deposition during night/morning. Methanol is known to be a sticky compound (Sect. 3.3), which is easily lost on surfaces, especially if they are wet (de Gouw and Warneke, 2006; Laffineur et al., 2012). Therefore, it is speculated that the early morning deposition could be caused by dew, which increases the surface deposition. Several studies observed similar patterns and/or suspected dew causing the deposition (Goldan et al., 1995; Riemer et al., 1998; Holzinger et al., 2001; Laffineur et al., 2012; Rantala et al., 2015; Wohlfahrt et al., 2015). The reason for the different durations of the depositions in Fig. 16 is most likely the earlier sunrise in Hyytiälä, which starts rising the ambient temperature and lowering the relative humidity. In Hyytiälä the methanol deposition made up 4% of the methanol emissions, while in Bosco Fontana the deposition amounted to 24% of the emission. This can be explained by the higher methanol concentration in Bosco Fontana. In Bosco Fontana the 24 h average methanol concentration was 14.3 ppb, while in Hyytiälä it was 4.3 ppb. Dew could also occur more often in Bosco Fontana, as it has a higher diurnal temperature gradient (10.1°C) compared to Hyytiälä (6.5°C). This gradient is caused by the longer nighttime in Bosco Fontana and the radiative cooling during the mostly clear nights.

Even though methanol is the second most abundant volatile organic compound in the troposphere and plays a significant role in atmospheric chemistry (Wohlfahrt et al., 2015), its global budget is very uncertain due to its bidirectional flux. Therefore, further measurements of methanol exchange are needed to improve and validate existing models.

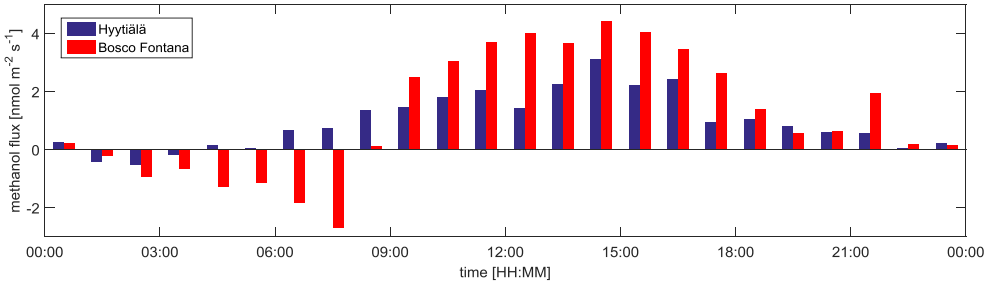

Figure 16: Methanol fluxes from Hyytiälä, recorded from the 01.06.2013 to the 24.06.2013, and Bosco Fontana, recorded from the 15.06.2012 to the 06.07.2012. Both ecosystems deposit methanol in the early morning and become methanol emitters during the day.

4.6 Sources of amines in animal husbandry

Amines are known to be very good at stabilizing clusters and therefore enable high nucleation rates already in low concentrations (Almeida et al., 2013). This enhancing effect of trimethylamine (TMA) in secondary aerosol formation has been found in various modelling studies (Murphy et al., 2007; Kurten et al., 2008; Petäjä et al., 2011; Paasonen et al., 2012). Therefore, one key target in the research barn in Switzerland (**paper I)** was the identification of the source of trimethylamine, the most emitted amine from cattle. VOC concentrations close to several potential sources have been measured. The sources included air exhaled by cows, air exhaled by ruminating cows, urine, feces and different fodder. The measurements proved challenging, as a clear separation of sources was often not possible due to the moving livestock. To follow cows in the parlor, a rather long inlet was necessary. The inlet was heated over 150°C and pumped with 80 L min^{-1} to reduce wall losses, as amines are known to be of low volatility and very sticky VOCs (Mikoviny et al., 2010; Sect. 3.3).

The measurements at the research barn showed that highest TMA concentrations were measured when feces and urine were mixed. To confirm these results, TMA emission measurements of urine, feces and a mixture of both were conducted over one week in a laboratory. These measurements showed that after 16 h the mixture of feces and urine had the highest emissions. This can be explained by the conversion of trimethylamine oxide (TMAO), found in urine, to TMA. The necessary microorganisms for this conversion are found in feces. Similar bacteria conduct the urea hydrolysis into NH_3 in the urine–feces mixture, which elevates the pH-value. In the alkaline environment, the TMA can then volatilize.

Overall, the mixing of urine and feces occurs mainly in animal husbandry, where animals are concentrated in small places with concrete floor. Therefore, TMA emissions will be highest in stables and yards, while on the open pasture urine and feces will not likely mix and the emissions will be smaller.

5 Review of papers and the author's contribution

Paper I investigates methods to measure trimethylamine and identifies the sources of trimethylamine from cattle. Measurements in a dairy cattle barn resulted in the identification of acetone and methane as respiration markers, while ammonia and TMA originated from animal excrements. Dynamic chamber measurements in a laboratory recorded highest emissions of TMA coming from an aging mixture of urine and feces.
I participated in the field measurements, analyzed the PTR-TOF data and contributed to the writing of the paper.

Paper II characterizes the VOC emissions from a Mediterranean oak forest. It compares two methods for finding total VOC exchange and investigates the chemical flux of methyl vinyl ketone and methacrolein caused by the oxidation of isoprene.
I was the main responsible person for the PTR-TOF measurements and practical organization of the University of Helsinki measurements in Bosco Fontana, analyzed the data of the PTR-TOF and wrote the major part of the manuscript.

Paper III compares the measured ecosystem flux from a Mediterranean oak forest with upscaled emissions based on leaf cuvette measurements. The differences of the isoprene and monoterpene fluxes measured by virtual disjunct eddy covariation (PTR-Quad) and eddy covariance (PTR-TOF) are also investigated.
I was the main responsible person for the PTR-TOF measurements and practical organization of the University of Helsinki measurements in Bosco Fontana. I helped with technical problems of the PTR-Quad at the measurement site, wrote the PTR-TOF measurement descriptions and commented on the manuscript.

Paper IV describes an in situ method for GC-MS to measure volatile organic acids in the ambient air. The new method is capable of measuring C2-C7 volatile acids with 2 h resolution. The acetic acid and propanoic acid concentrations are compared with PTR-TOF results.
I measured and analyzed the PTR-TOF data and contributed to writing the parts concerning the PTR-TOF concentrations and commented on the manuscript.

Paper V investigates the temporal variations of VOC fluxes above a boreal forest. EC ecosystem fluxes from April, May and June and the development of the total emission, as well as the variation of compounds with exchange are reported. Comparisons with other EC flux studies were made, as well as with the long term SLP fluxes in Hyytiälä.
I was the main responsible person for the PTR-TOF measurements during the field campaign and analyzed the major part the data. I wrote most of the manuscript.

6 Conclusions

In this study the overall performance of a PTR-TOF was investigated, especially its reliability for EC flux measurements in different ecosystems. Eddy covariance measurements in a broadleaf forest in Italy (**papers II** and **III**) resulted in a net exchange of 9.8 nmol m^{-2} s^{-1}. The emissions in this oak forest were dominated by isoprene, while the deposition was dominated by methanol. In the conifer forest in Finland (**paper V**), the net exchange was 2.3 nmol m^{-2} s^{-1}. Here methanol was dominating the exchange, the group of monoterpenes being the major terpene source. Over 20 additional VOCs were emitted by both ecosystems (**papers II** and **V**). At both sites methanol showed a clear diurnal pattern with deposition in the mornings and emissions during the day. This emphasizes the role of dynamics in biosphere atmosphere interaction, where, depending on the environmental conditions (e.g. temperature, RH), emission can change into deposition.

These EC fluxes were then compared with vDEC exchange measured by the PTR-Quad (**paper III**) as well as with the profile method using PTR Quad (**paper V**). Overall, the major flux compounds above the two ecosystems agreed reasonably well: isoprene and monoterpene fluxes in Bosco Fontana (**paper III**) measured by the two methods had similar variations, resulting in correlation factors of 0.95 and 0.71, respectively. The average flux showed a 50% difference. At SMEAR II (**paper V**) the two exchange measurements showed average fluxes within 10% for methanol, acetone and monoterpenes, while the correlation, due to low data coverage, varied between 0.07 and 0.6. For fluxes close to the detection limit or influenced by fragmentation, the discrepancies in the comparisons were up to tenfold and, therefore, very uncertain. The connection between plant cuvette emissions and the ecosystem exchange was investigated in **paper III**. Overall, the comparison looked promising, but further research is still needed. To improve the results, more leaf emissions from different parts of the canopy and from several trees of the same species from different location in the forest would be needed. Additionally, if more than just isoprene and monoterpenes would be upscaled, more complex air chemistry would have to be included.

All presented exchange data were analyzed using a new, automated method to classify flux compounds in the PTR-TOF data (Park et al., 2013). This method was tested and compared with the manual method, where the CCFs are manually inspected for maxima (**paper II**). The manual method is very work intensive, as several thousand CCFs must be checked and classified. The automated method was faster, more objective and found more compounds with exchange and, therefore, was recommended and was used in the EC studies in this thesis.

The presented measurements are affected by many interferences, ranging from oxidation below the inlet of the instrument creating artificial fluxes to the inlet losses and fragmentation in the instrument. In **paper II** the isoprene oxidation between the emission and the measurement inlet has been studied. Model calculations showed that this led to an underestimation of the isoprene flux by up to 5%. This oxidation, however, could explain up to 30% of the methyl vinyl ketone / mathacrolein exchange. In **paper IV** ambient concentrations of

volatile organic acids were measured. The main acid measured with the PTR-TOF was acetic acid, which showed six times lower concentrations than the GC measurements. A memory effect was identified, where the instrumental background followed the ambient acetic acid concentration, thereby reducing the measured concentrations. The source for the butene emissions in Hyytiälä has been investigated (**paper V**). During the measurement campaign, which lasted from April to June, the emissions were highest in April, which indicated an anthropogenic source. As the highest emissions came from places where aerosol measurements were positioned and butene is reported to be a major fragment of butanol, the conclusion was made that the measured butene emissions are actually caused by the evaporation of butanol from the condensation particle counters.

The source of the major amine emitted from animal husbandry, trimethylamine, was identified. During measurements at the research stable in Switzerland (**paper I**), the highest concentrations of trimethylamine were measured when urine and feces are mixed and left to age. This result was confirmed in the laboratory using dynamic chamber measurements. Interestingly, this means, that the amine emissions increase in enclosed (e.g. animal husbandry) and are lower when the cattle are on the meadow, where urine and feces are unlikely to mix. These results are important as those anthropogenic amines have the ability to amplify the nucleation rate and create a lot of clusters, increasing the number of particles, which can, under favorable conditions, grow to cloud condensation nuclei and affect climate.

This thesis shows that PTR-TOF is capable of measuring EC exchange over different ecosystems and can provide new insights into the biosphere-atmosphere exchange and air chemistry. The ability to measure whole VOC spectra in 10 Hz time resolution gives the PTR-TOF a clear advantage to the PTR-Quad instruments. However, these traits come with its drawbacks. The high amount of data, which are collected with a PTR-TOF, are challenging to analyze, and the calculation of VOC fluxes is, therefore, time consuming.

The data from this work can be used to refine air chemistry models and help to further increase the knowledge of the fate of VOCs and the formation of aerosol in our atmosphere. Especially VOCs like amines or oxidation products of monoterpenes have a high potential to form and grow aerosol that can affect climate. Still, more measurements of total VOC exchange from different ecosystems are needed to better estimate global VOC budgets, and improve global emission models.

In the future, more sensitive mass spectrometers, such as PTR3 (Ionicon Analytik GmbH) and Vocus PTR-TOF (Tofwerk AG) with better limits of detection, will be able to measure even smaller fluxes and concentrations, pushing the boundaries to detect fast reacting and highly oxidized VOCs. These instruments could be able to measure terpenes as well as their oxidation products and the first clusters. Although new insights can be found with these instruments during work intensive measurement campaigns, simpler and more robust instruments are also needed for long term observations of VOC concentrations and fluxes in remote places.

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